OneD™ material

# Innovative Cell Materials and Design for 300 Mile Range EVs

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Palo Alto, California
June 16 ~20, 2014

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# Overview

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## Timeline

- Start: Oct. 1st, 2011
- End: Sept. 30th, 2014
- 75% complete

## Budget

- Total project funding: $8,060K
  - DOE share: $4,840K
  - Contractor share: $3,220K
- Funding received in FY13: $1,500K
- Funding for FY14: $1,931K

## Barriers

- **Barriers addressed**
  - Performance: Low Wh/kg & Wh/L
  - Life: Poor deep discharge cycles
  - Cost: High $/kWh
- **Targets**

| | | | | | |
|---|---|---|---|---|---|
| **Anode:** | >700 mAh/g | | 1,600 mAh/g | >800 cycles |
| **Cathode:** | 250 mAh/g | ➡ | >260 mAh/g | >800 cycle |
| **Cell:** | 350 Wh/kg | ➡ | 800 Wh/L | <150 $/kWh |

## Partners

- Interactions/ collaborations

A123 Systems, LGCPI/LG Chem. & other cell manufacturers

US DOE National Laboratories

University of California, Berkeley

Cell components manufacturers

# Project Objectives

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## The review covers Apr. 2013 ~ Mar. 2014

**Anode:**

Develop a 700~1600 mAh/g Si anode (SiNANOde™) toward >800 cycles

- 700~1000 mAh/g SiNANOde toward >800 cycles
- 3~6mAh/cm2 SiNANOde
- 1600 mAh/g SiNANOde

**Cathode:**

Develop a 260 mAh/g cathode (Mn-rich) toward >800 cycles

- Improve 250~260 mAh/g cathode loading, power and cycle life
- Develop 3~6mAh/cm2 electrode (1-side) using well-established materials

**Cell:**

Develop unique cell combining SiNANOde with selected cathode to achieve

- Cell design toward 350 Wh/kg and 800 Wh/L
- Feasibility test using single layer pouch cells
- Pouch cells resulted in <150 $/kWh (cell) (delivered the cells for testing at INL)

# Project Milestone

**Milestones in the period of Apr. 2013 ~ Mar. 2014:**

- Baseline SiNANOde Cycle Life Demonstration
- SiNANOde Specific Capacity up to 700~1600mAh/g with improved cycle life
- Optimization of cathode  composition
- Scale-up SiNANOde manufacturing process

**Overall Project Milestone Status**

| | | |
|---|---|---|
| **Kick off meeting** | **10/26/11** | **Completed** |
| **1st quarterly report** | **1/31/12** | **Completed** |
| **Initial Specifications Complete** | **10/31/11** | **Completed** |
| **Material Properties Modeled** | **12/30/11** | **Completed** |
| **Anode material batch deliveries and characterization** | | **Multiple On track** |
| **Cathode material batch deliveries and characterization** | | **Multiple On track** |
| **Test Cell** | | **Multiple On track** |
| **Delivered year 2013 high energy density cells on 1/10/14** | | **On track** |
| **Systems Integration Design** | **9/31/12** | **On track** |
| **Test Reports Delivered to DoE** | **Multiple** | **On track** |

# Drop-In Anode Solution

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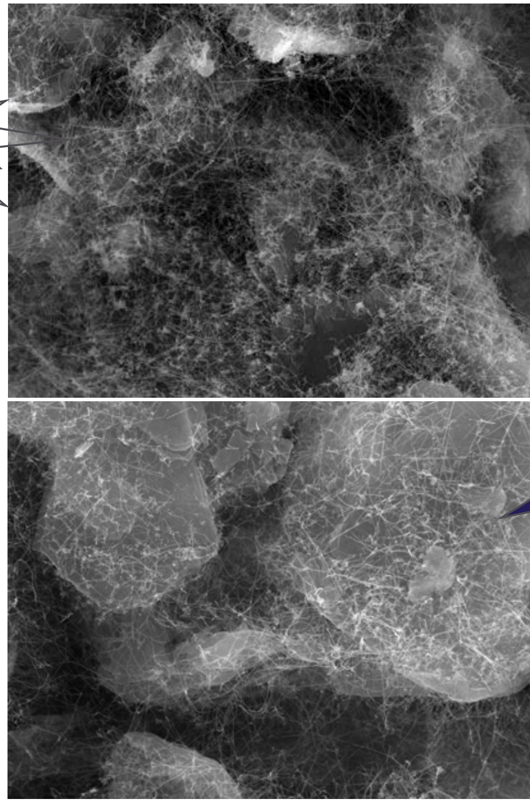
High Capacity



Similar feel to graphite, e.g. tap density similar to graphite powder substrate

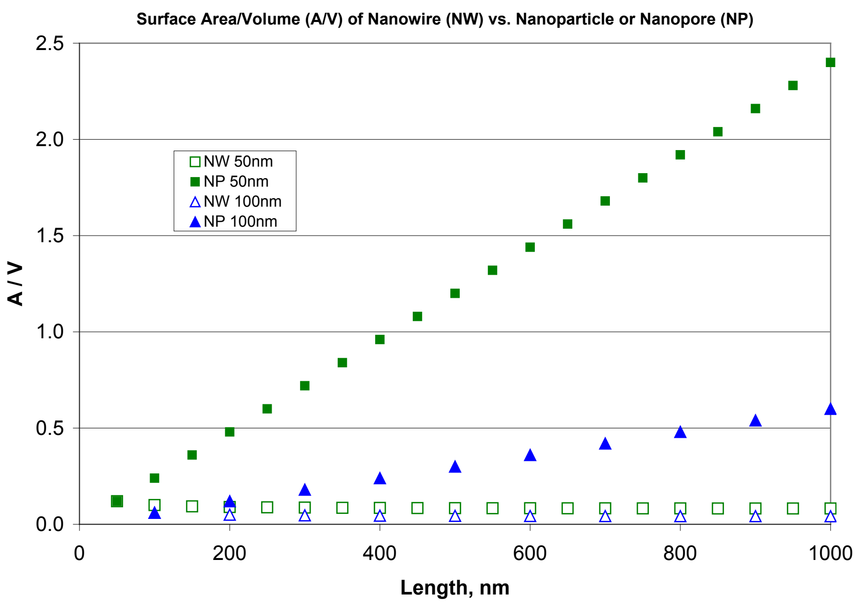
Volume production process using graphite as direct substrate for Si nanowire growth

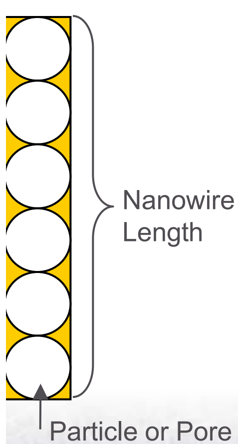
- Cost effective and high Si utilization
- Improves dispersion within slurry and drop in process
- Si-C conductivity improvement
- Si% or anode specific capacity is controllable, focusing on **500 ~ 1600 mAh/g**
- High electrode loading, i.e. 1.5g/$cm^3$
- Good cycling performance, cycled >1000 times

# Anode Approach

## SiNANOde vs. Hollow/Porous Approach

| Nano-material Advantages | | Overcome Disadvantages of Nano-material | SiNANOde | Hollow/Porous Si |
|---|---|---|---|---|
| Better accommodation of cycling strain<br>Unique conversion reactions | | High surface area leads to higher self discharge & poor cycling performance | Low A/V & Intact NW after cycling | High A/V; defects |
| High interfacial charge transfer rates<br>Short tunneling length for electronic transport | | Low pack density and low volumetric energy density | Pack density similar to graphite | Pack density lower than graphite |
| Short diffusion length for ionic transport | | Hard to be mass-produced | Mass-produced with a competing cost * high Si utilization | Difficult and expensive to commercialize |




The nanowire has lower surface area/volume ratio, A/V, and hence less side-reaction with electrolyte and better cycle life

# Cathode Approach

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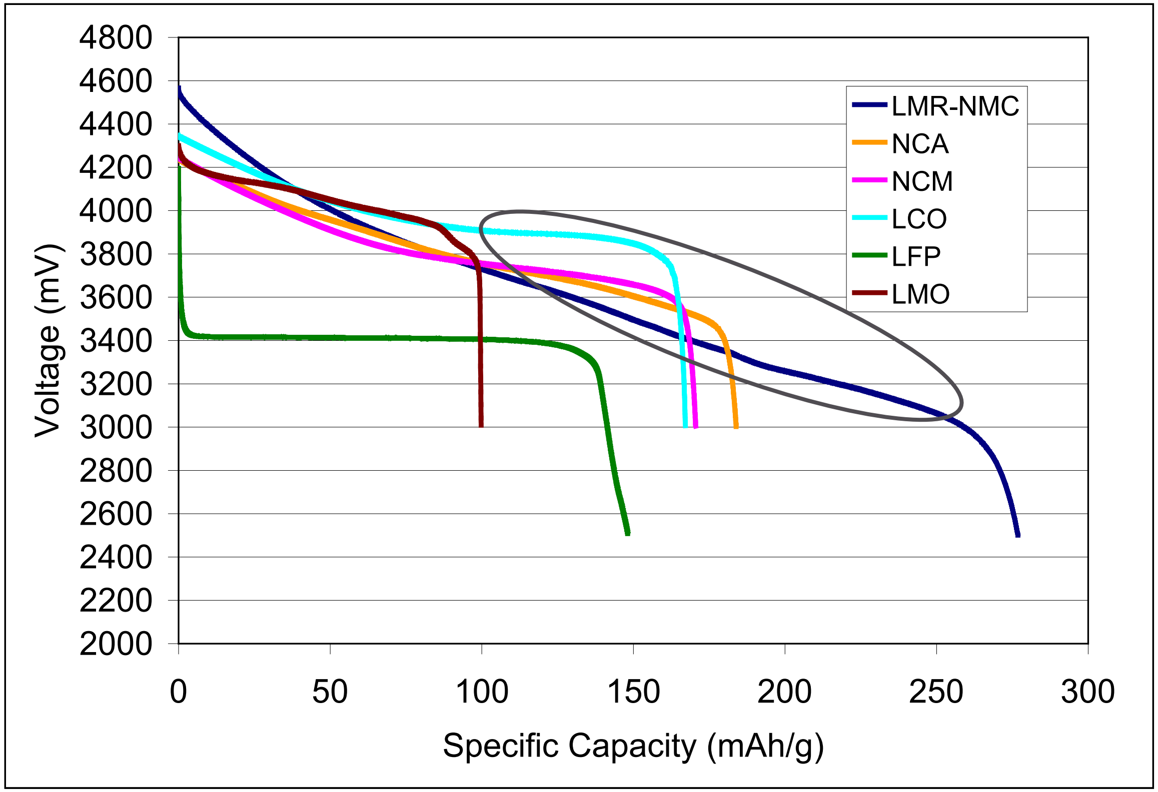


LMR-NMC >250 mAh $g^{-1}$, requesting high voltage electrolyte

- Mn-rich cathode materials are screened and combined with SiNANOde
- Single side loading 3~6 $mAh/cm^2$

LCO, NCA or NCM 160~200mAh/g, utilizing conventional electrolyte

- Lowering inactive material content down to 4~5%
- Single side loading 3~6 $mAh/cm^2$

# Cell Development Approach

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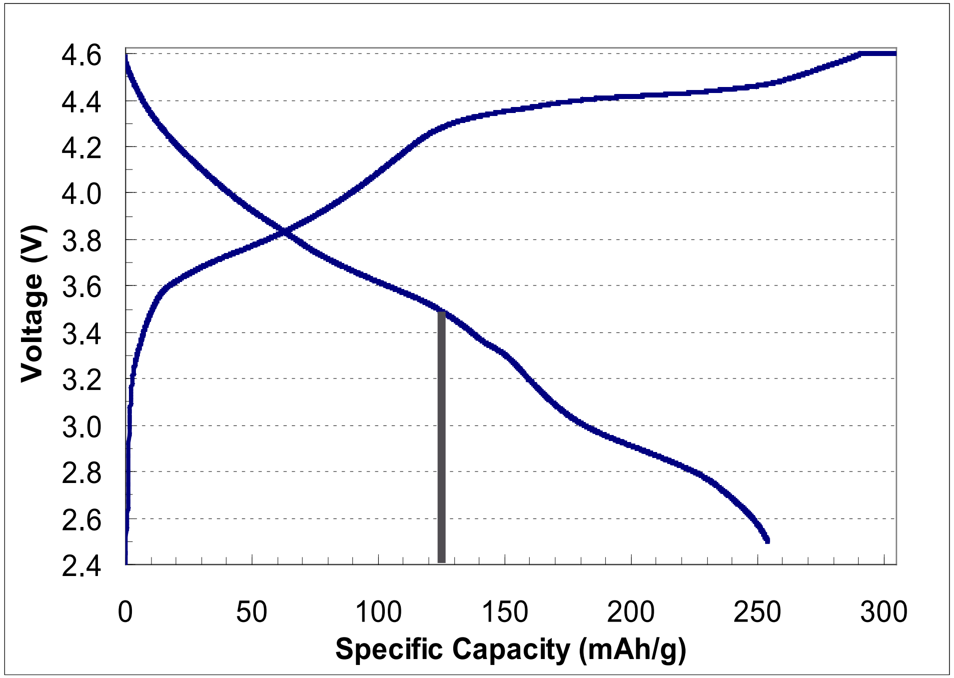
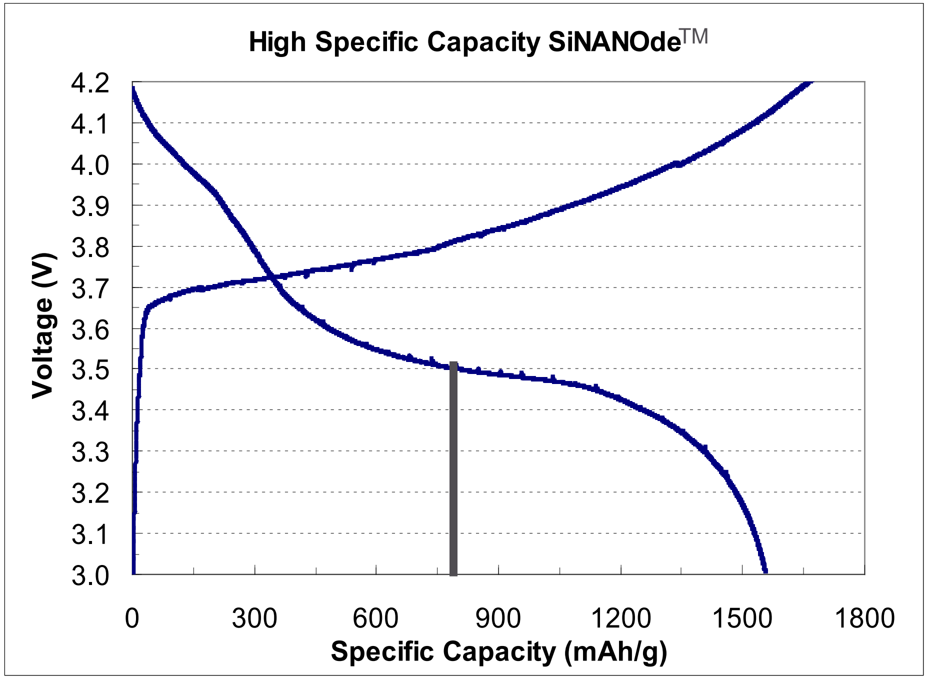
## Combining the attractive cathode feature with a high-capacity SiNANOde

### SiNANOde/LMR-NMC




### SiNANOde/LCO




SiNANOde/LMR-NMC full cell showed a ICE of 83.6%, which realized a reversible specific capacity of 255mAh/g for the cathode

But its discharge voltage is ca. 3.5V at 50% DOD when the cell is cycled in 2.5 ~ 4.6V

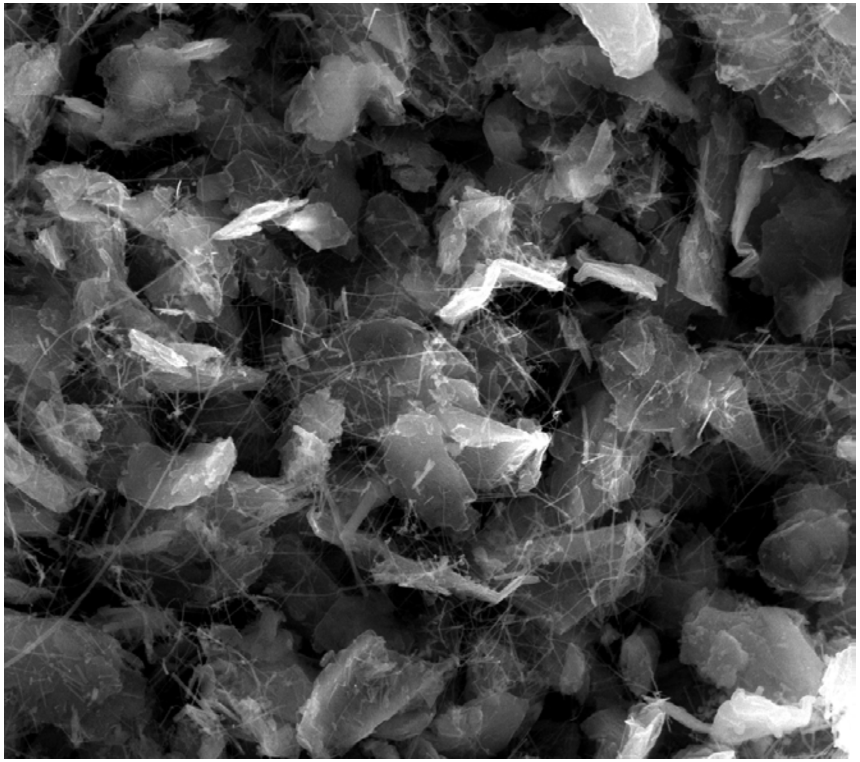
Request high voltage electrolyte

SiNANOde/LCO full cell showed a high ICE of >91% while the SiNANOde had a specific capacity of 1600mAh/g

It discharge voltage is ca. 3.5V at 50% DOD though the cell is cycled in 3~4.2V

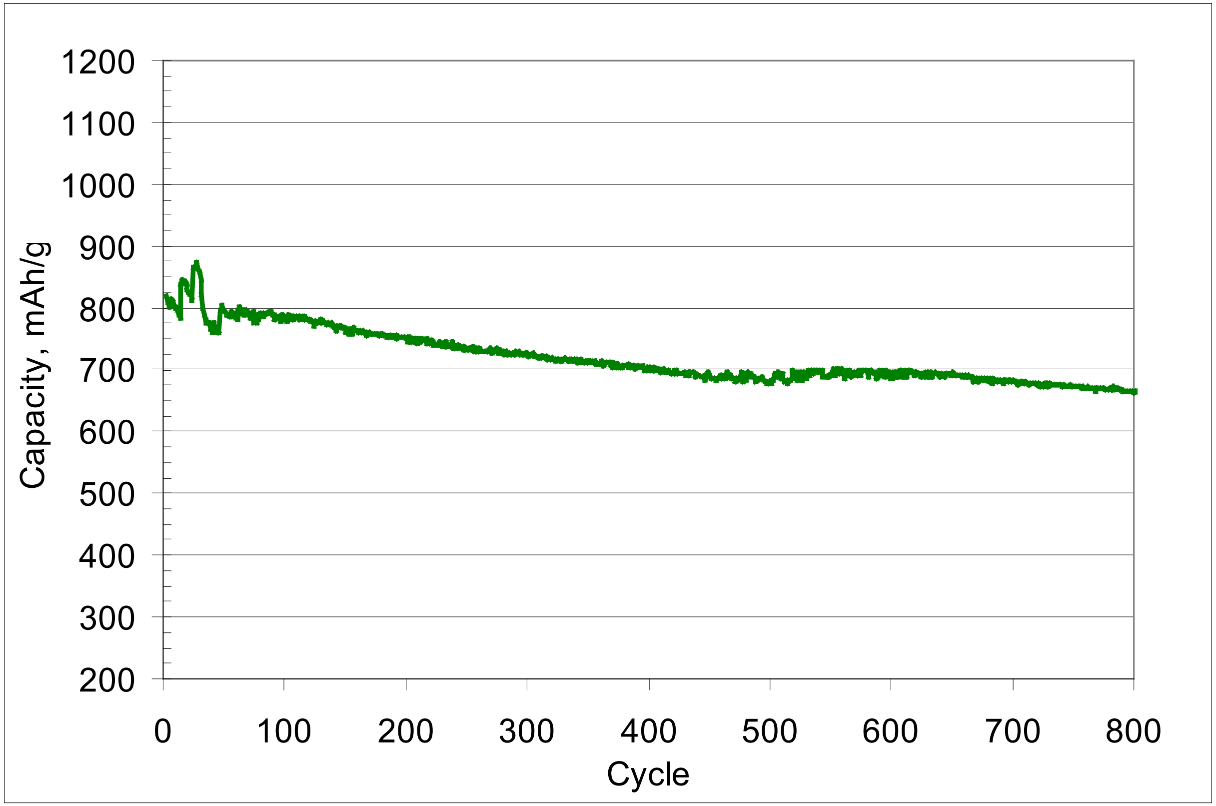
Utilize conventional electrolyte

# Technical Achievement
## - Low Cost SiNANOde



Zero-Au SiNANOde development on different graphite and carbon substrate powders has been extensively explored, which results in a wide range of tunable Si nanowire density on the substrate powders. Smaller powders have higher surface area that can host more Si nanowires. Si nanowire content can be as high as 50% in the SiNANOde composite, corresponding to a specific capacity of >2000 mAh/g.

# Technical Achievement
## - High Capacity Anode: Cycle Life




**- Up to 850mAh/g SiNANOde by controlling Si nanowire content.**
**- Continuously improving its conductivity and optimizing electrolyte, which has showed longer cycling life of ~800 cycles at 79% capacity retention at 0.3C cycling in the half cells.**
**- At beginning the cell has been used for various C-rate testing.**

# Technical Achievement

## - High Energy Density Pouch Cell Performance

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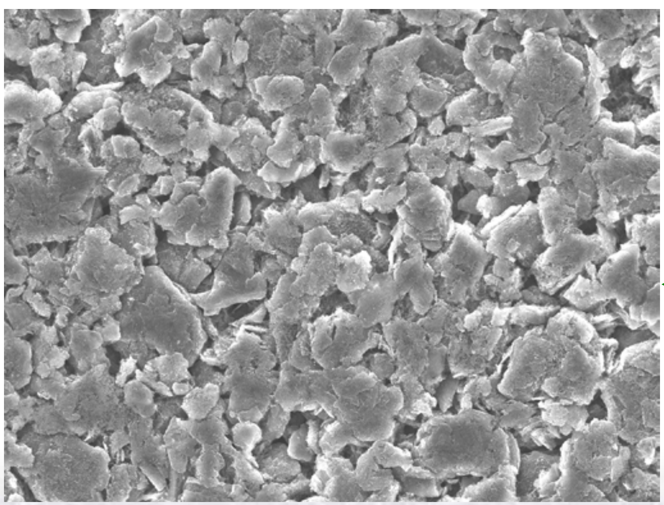
| Discharge C-rate | Energy Density Wh/L |
|---|---|
| C/10 | 627 |
| C/5 | 616 |
| C/3 | 582 |

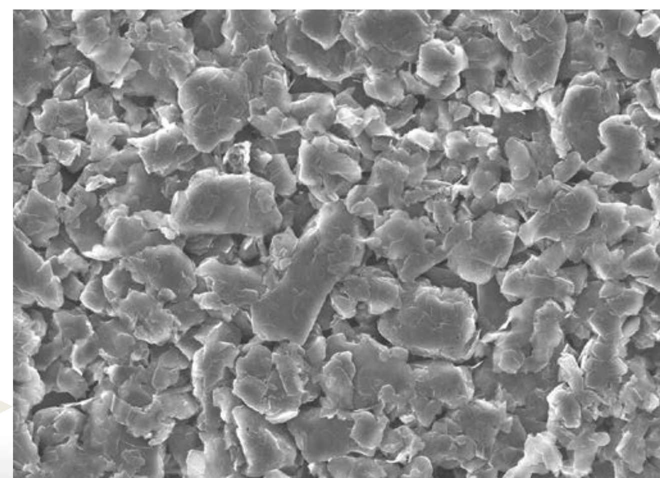
- The 8%SiNANOde pouch cell has already showed the volumetric energy density **>620Wh/L** in conventional 4.2 ~3.0V.
- The mid-voltage is ~3.7V.



**Calendered Anode**
**~1.5g/cm$^3$**

**SiNANOde** ←

**Graphite** →



# Technical Achievement
## - Less Voltage Hysteresis for SiNANOde

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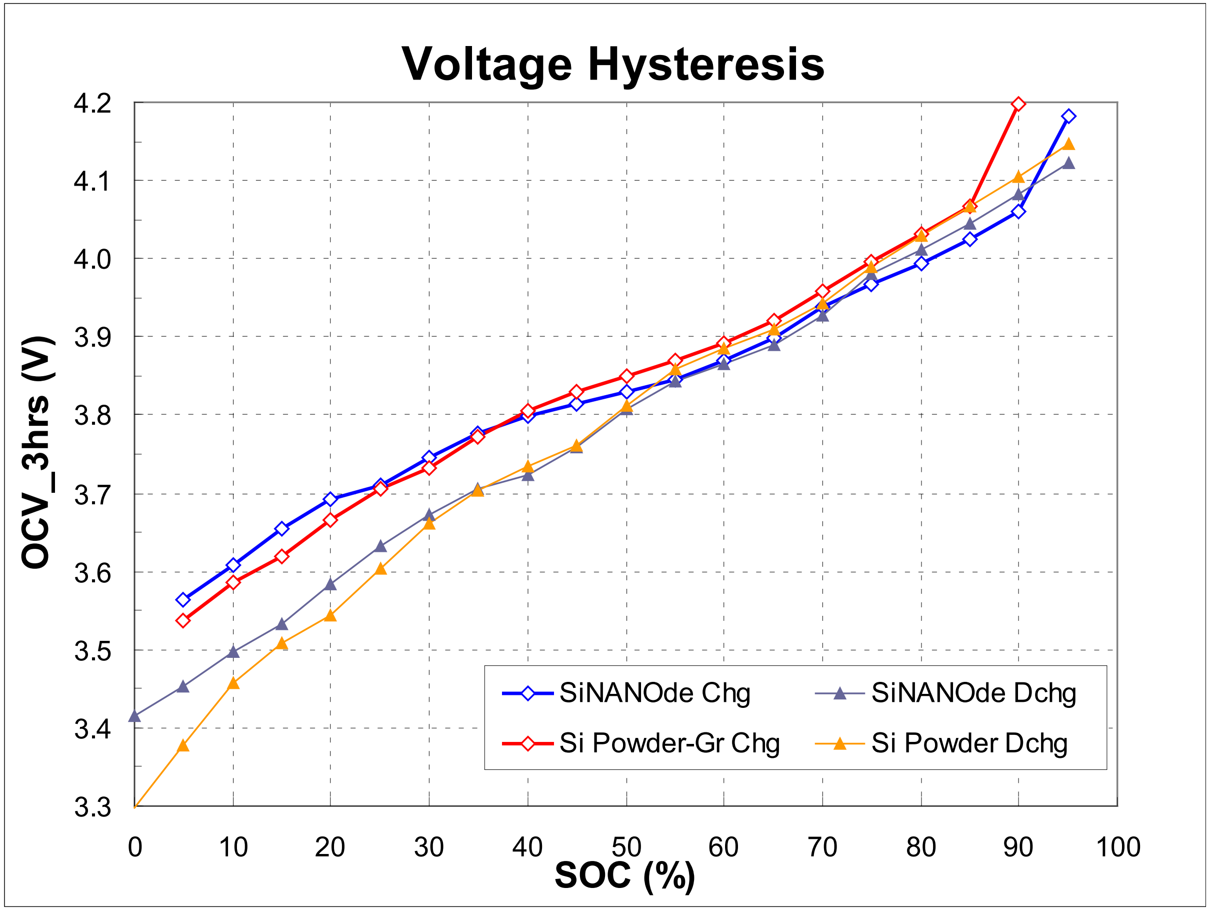
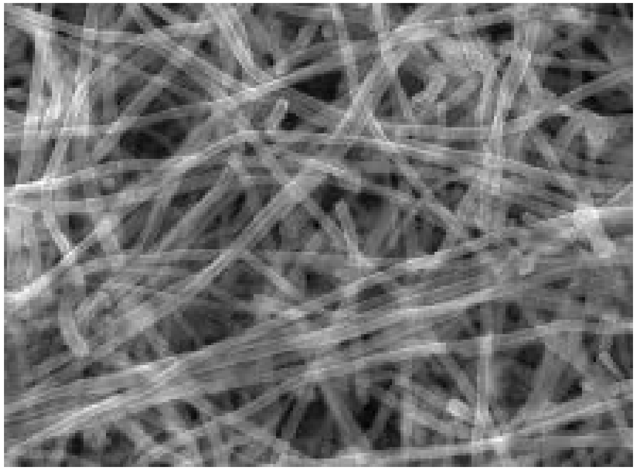
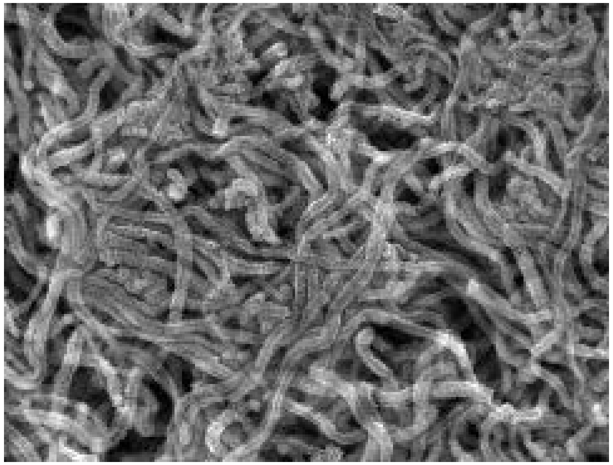



The hysteresis effect is less pronounced for 8%SiNANOde/LCO full cell in comparison with 8%Si powder-graphite/LCO full cell

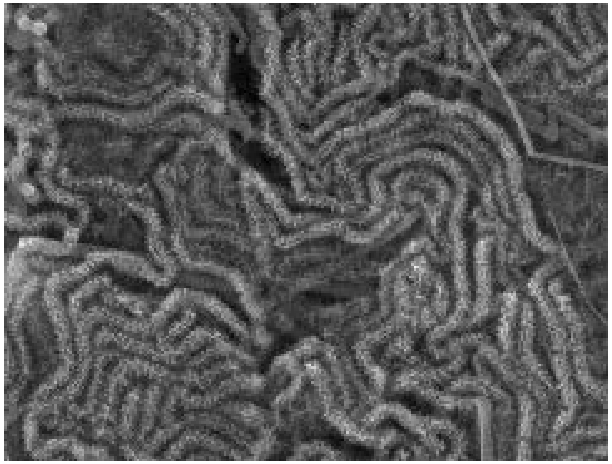
# Technical Achievement
## - SEM of Si Nanowires/Current Collector Post Cycling



**Prior to cycling**



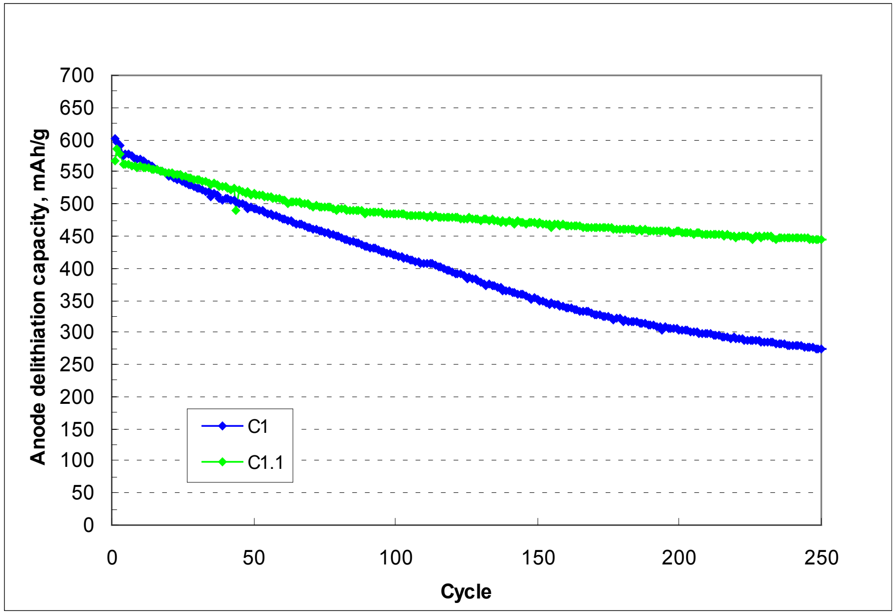
**10th cycle**

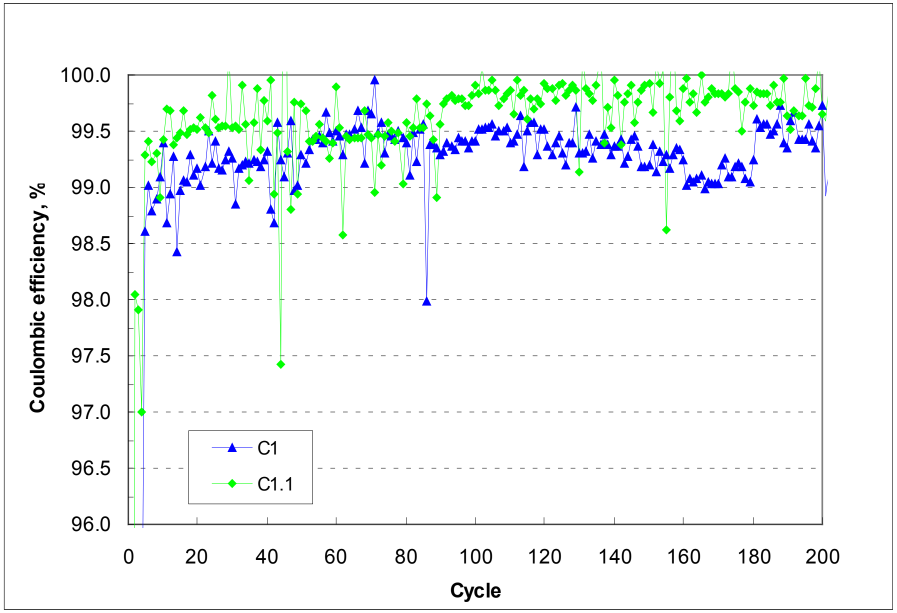


**100th cycle**

- Si nanowire deforms to fill void areas in carbon anode material matrix
- Si nanowire remains intact and fully functional after 100% DoD cycling
- Thin SEI formed on Si nanowires

# Technical Achievement
## - SiNANOde SEI in OneD's C1 & C1.1 Electrolyte



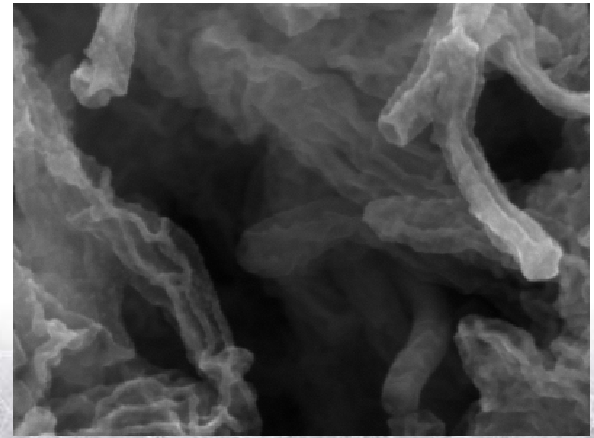




- C1.1 cell showed higher coulombic efficiency and better cycling performance than C1 cell

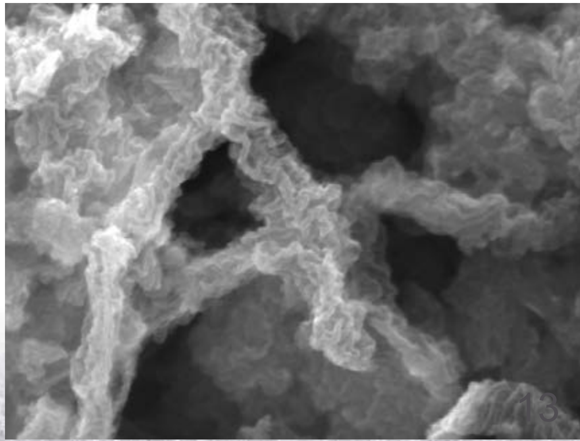
**- In C1: the Si nanowires in the composite can be deteriorated faster and formed thicker SEI**

**- In C1.1: thin SEI or less decomposed electrolyte buildup on Si nanowires in the composite**

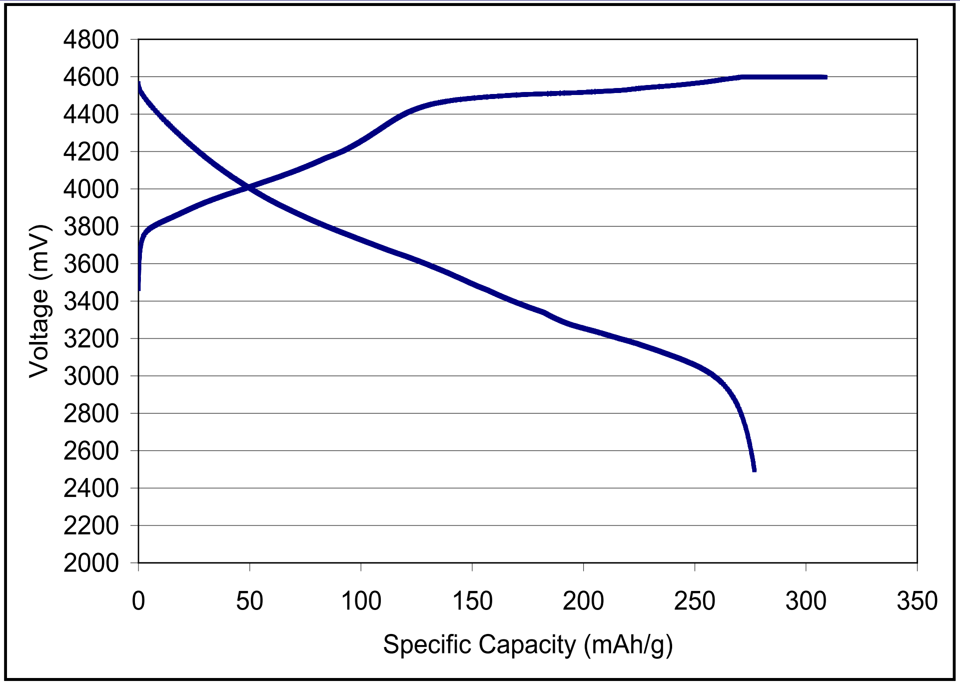
**C1.1**

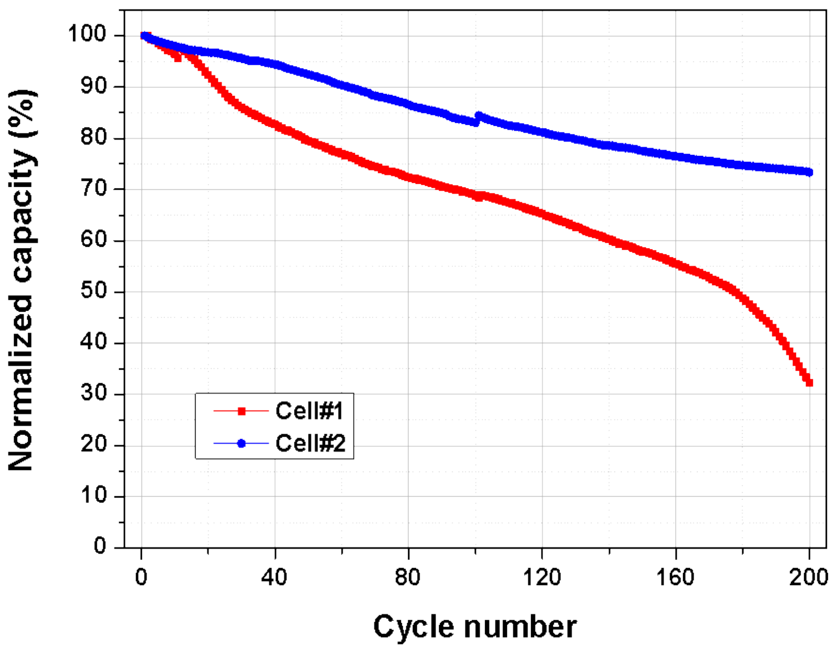


**C1**



# Technical Achievement
## - Cathode




**Mn-rich cathode materials showed a reversible specific capacity as high as 275mAh/g**

**But its discharge voltage is ca. 3.55V at 50% DOD when the cell is cycled in 2.5 ~ 4.6V**

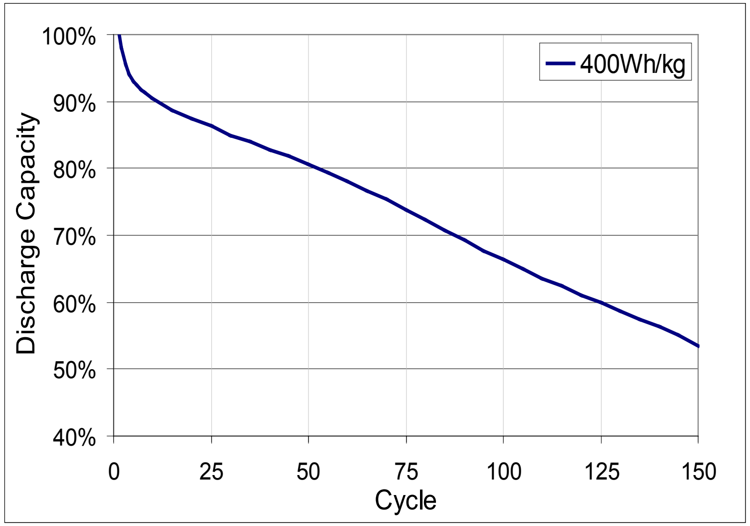
**Request high voltage electrolyte**

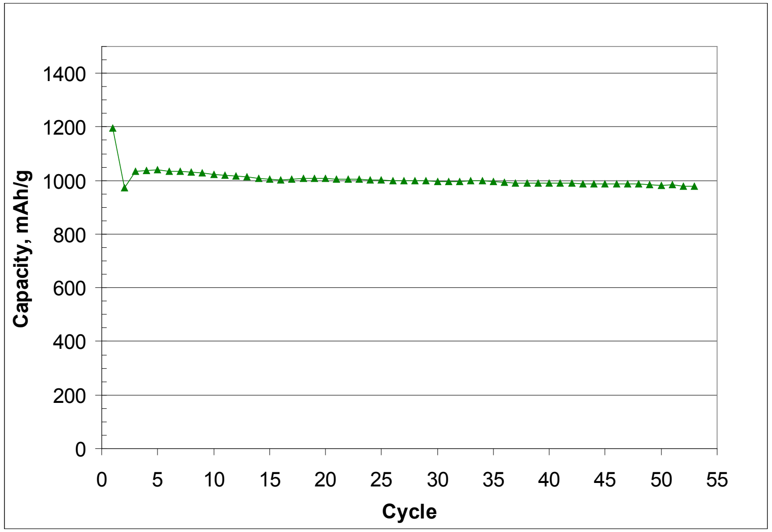
**- A high voltage electrolyte can enhance cycle life of the LMR-NMC.**
**- The tailored electrolyte composition used in Cell #2 exhibits high voltage stability.**

# Technical Achievement
## - Cell Development

To achieve high energy densities in SiNANOde/Mn-rich cathode pouch cells, the cell fabrication processability in plant has been evaluated

| SiNANOde | 600 mAh/g | 800 mAh/g | 1200 mAh/g |
|---|---|---|---|
| Processable in plant 4.4 V | 225 Wh/kg | 240 Wh/kg | 255 Wh/kg |
| Unprocessable → processable in plant 4.4 V | 255 Wh/kg | 275 Wh/kg | 300 Wh/kg |



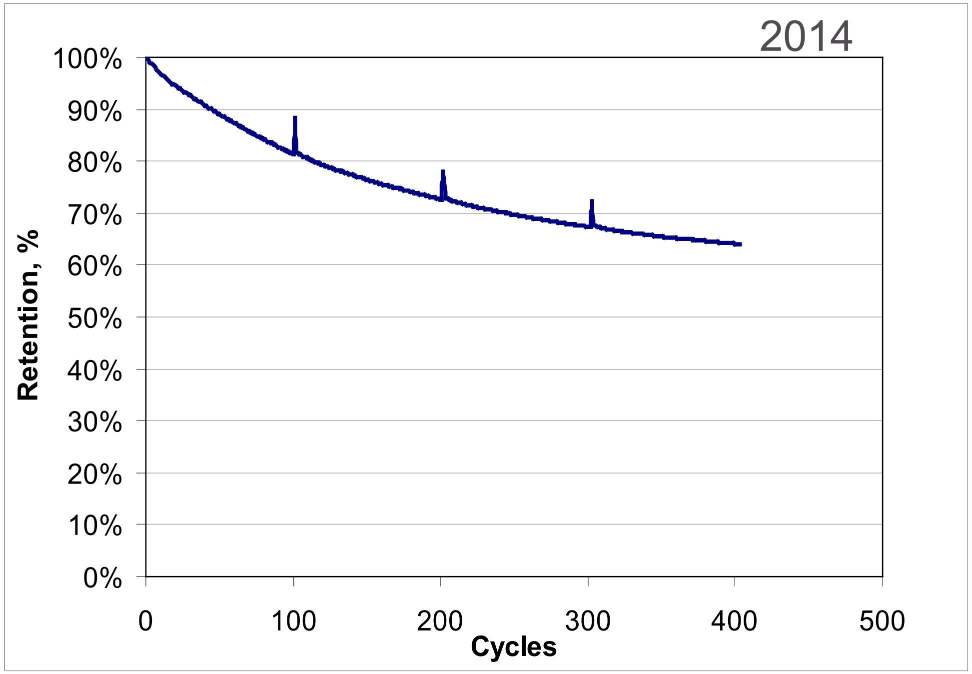

The manually-made 400 Wh/kg cell is cycled at 0.3C. The capacity is initially fading faster, showing 55% retention at 150th cycle

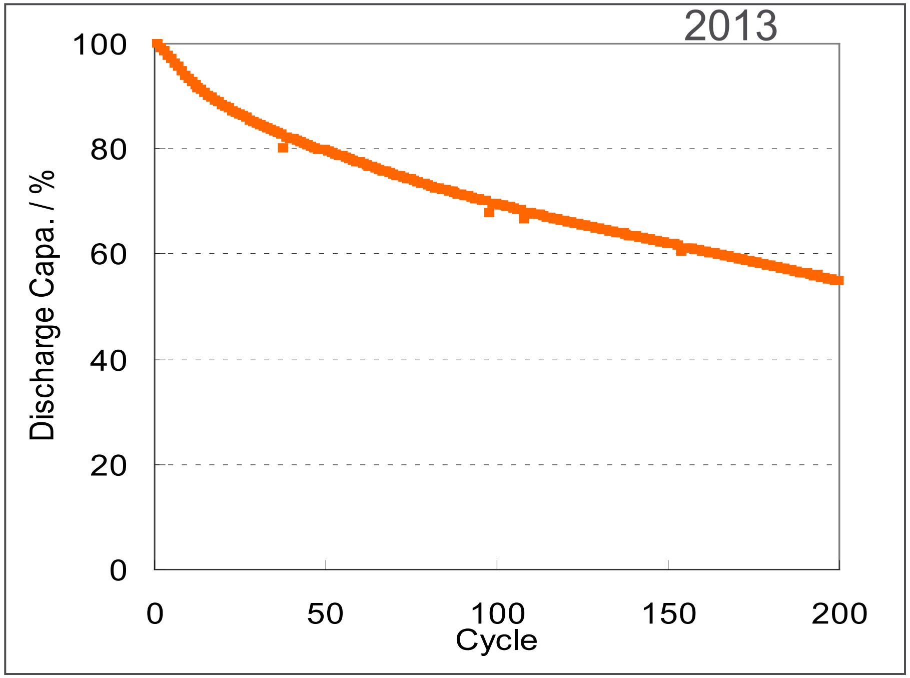
The 1200 mAh/g SiNANOde processability has been improved and hence showed stable cycling performance.

# Technical Achievement
## - Cell Development

***1.3 Ah pouch cell with 600 mAh/g anode and LCO cathode, achieved >260 Wh/kg and >600 Wh/L in 2013 but it has not been well cycled in 4.3 ~ 3V.***

***Similar pouch cell with 600 mAh/g anode and NCA cathode has been cycled for 400 times above 62% retention in 4.3 ~ 3V though its cycling performance is still worse than that in 18650 cell (Next Slide)***




The cell is Cycled at 0.5C rate (DOD 100%)

# Technical Achievement
## - Full Cell Cycling Behavior: SiNANOde vs. Graphite

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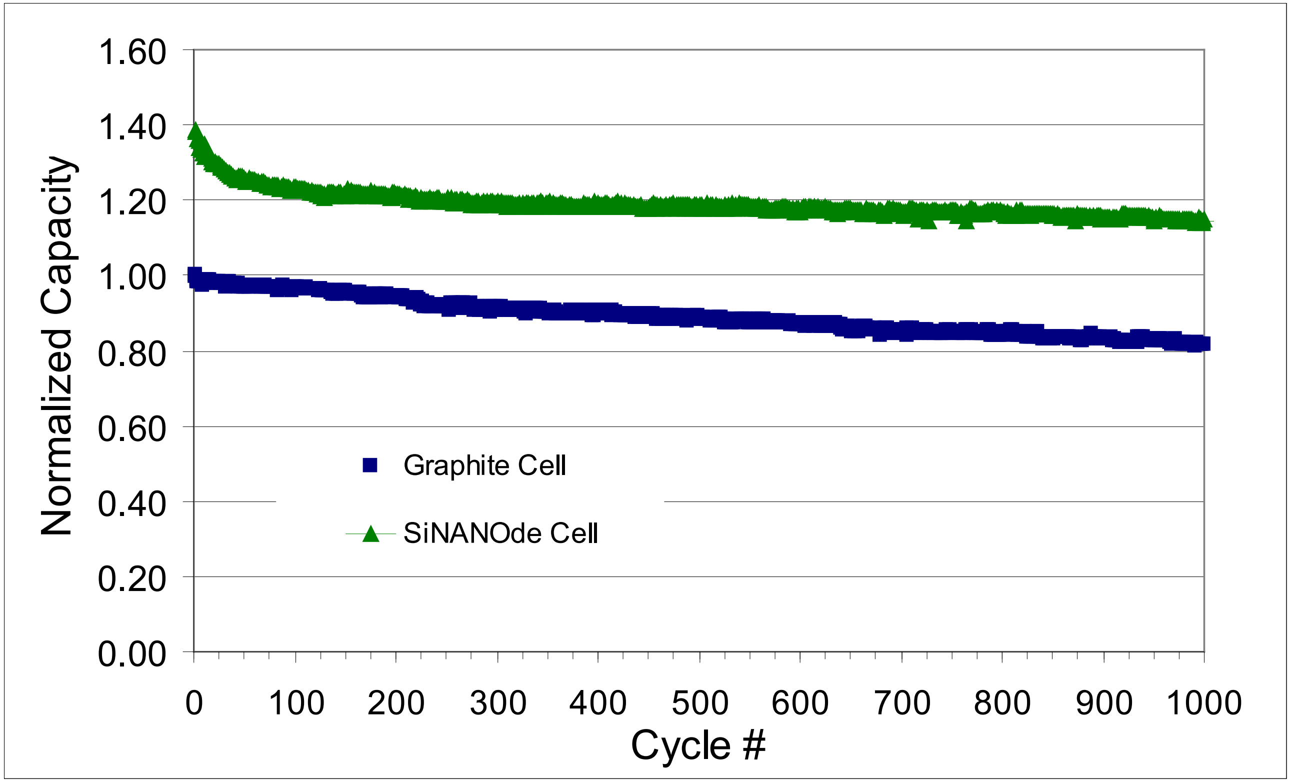
### Superior full cell performance at high electrode loading




Cylindrical full cell cycling behavior:
- Commercial graphite cell can be cycled 1000 times at 81% capacity retention.
- SiNANOde/NCA cell exhibited a faster decay in the first 100 cycles but it still has a 82% capacity retention at 1000th cycle, which also showed higher anode-specific capacity over graphite anode.

# Pouch Cell Cycle Life
## – High Capacity SiNANOde/LCO

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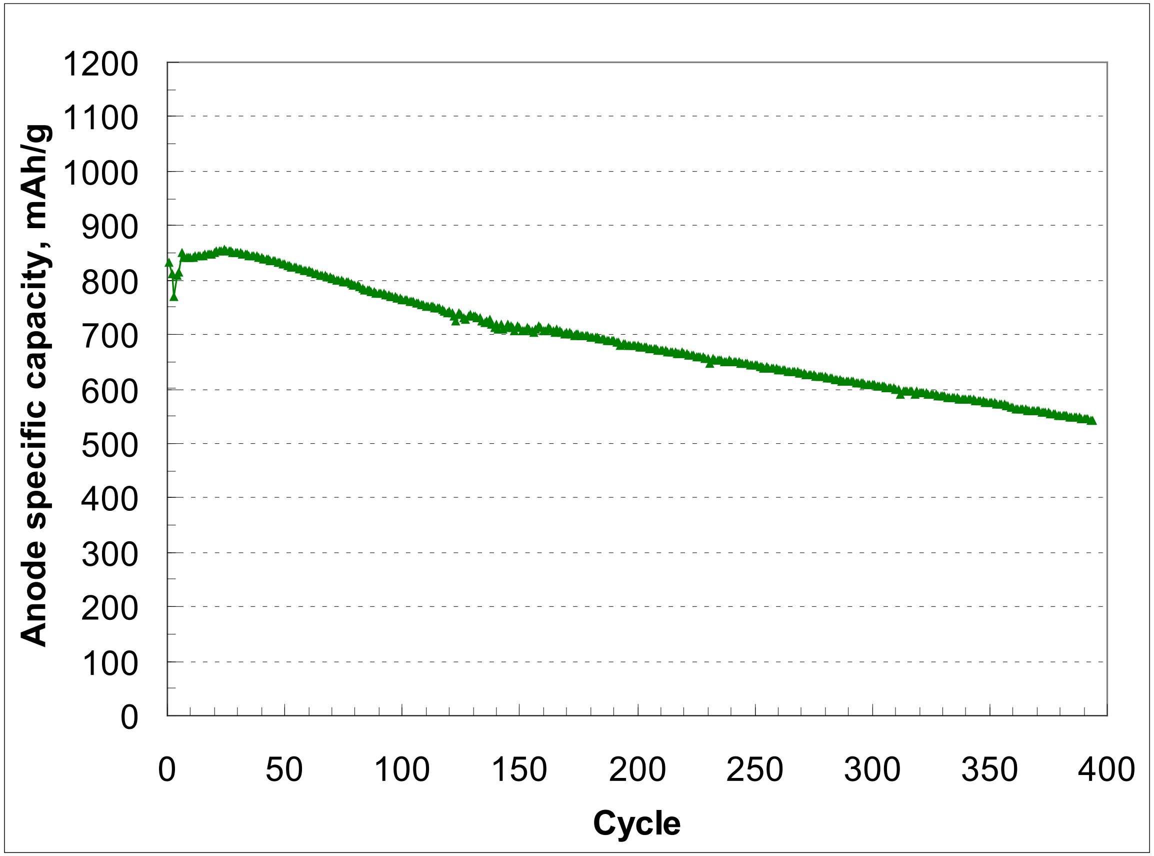


- High capacity SiNANOde pouch cell has achieved a reversible capacity of ~ 850mAh/g.
- Coulombic efficiency is >99.9%, which has showed better cycling life at +0.3C/-0.5C for the pouch cell, 210 cycles at 80% and 330 cycles at 70% retention.

# Technical Achievement

## - Low Temperature Performance for Pouch Cells at C/2

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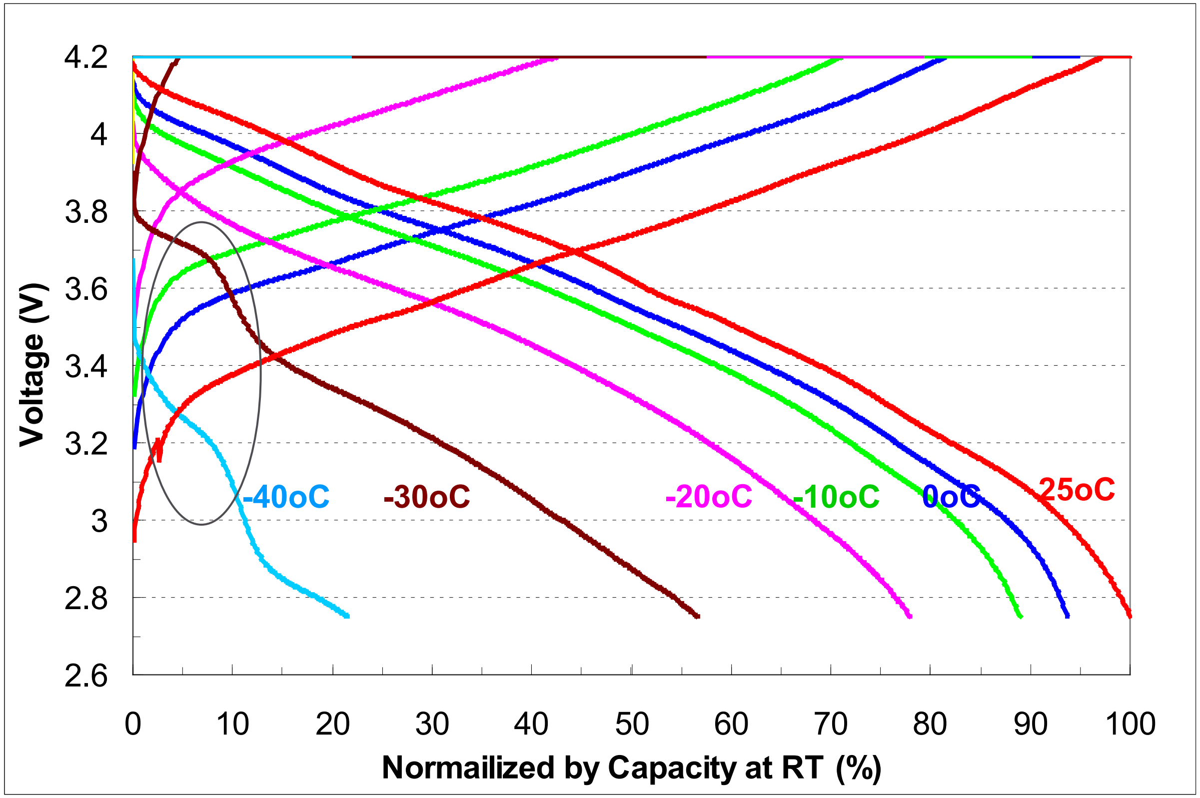
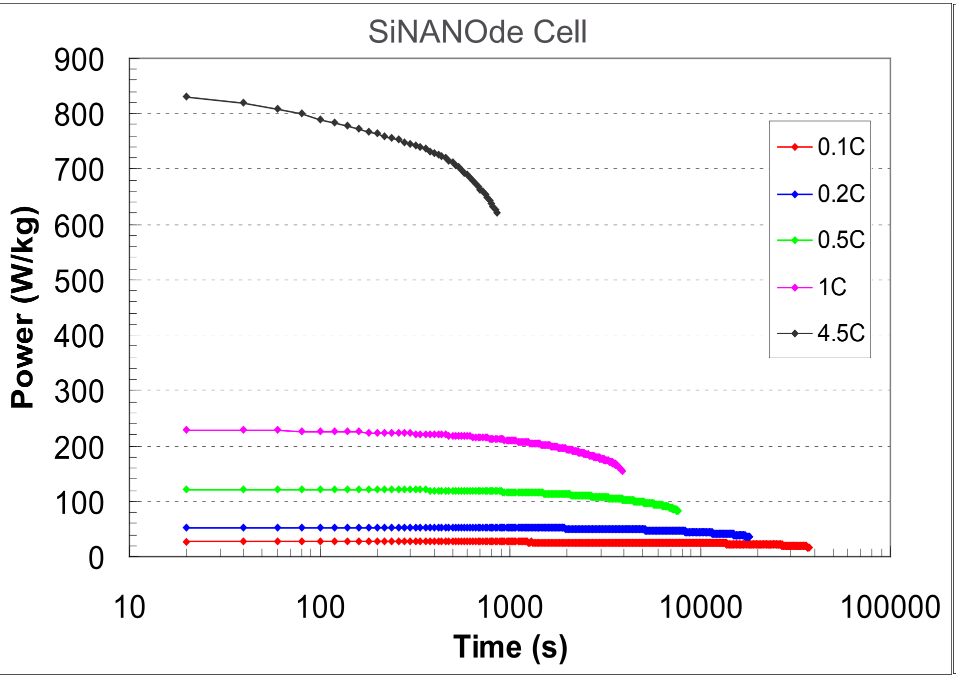
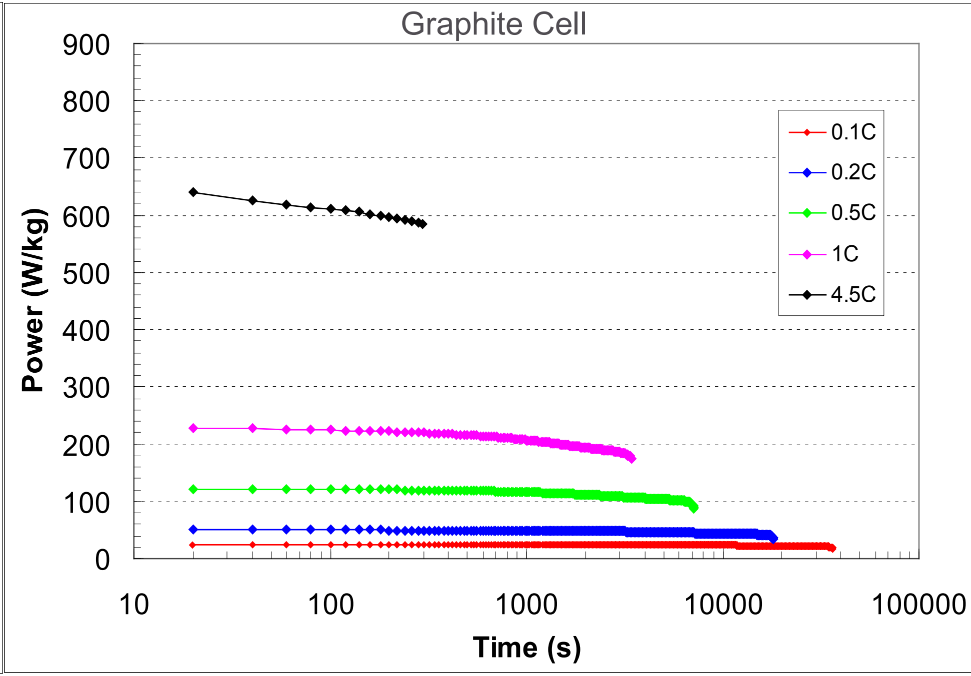
SiNANOde pouch cell was charged and discharged at the same temperatures




- At 25°C ~ -20°C, SiNANOde pouch cell showed a typical temperature-dependent performance similar to graphite pouch cell.
- Even at -30°C, SiNANOde cell can be charged at C/2 for 5% prior to 4.2V while graphite cell can not be charge at C/2 as the cell voltage jump to 4.2V for CV charge. SiNANOde cell exhibited two discharging steps at -30 ~ -40°C, indicating that it has potential to be discharged at higher voltage if extending the first step (further investigation is ongoing).

# Specific Power of High Energy SiNANOde Pouch Cells



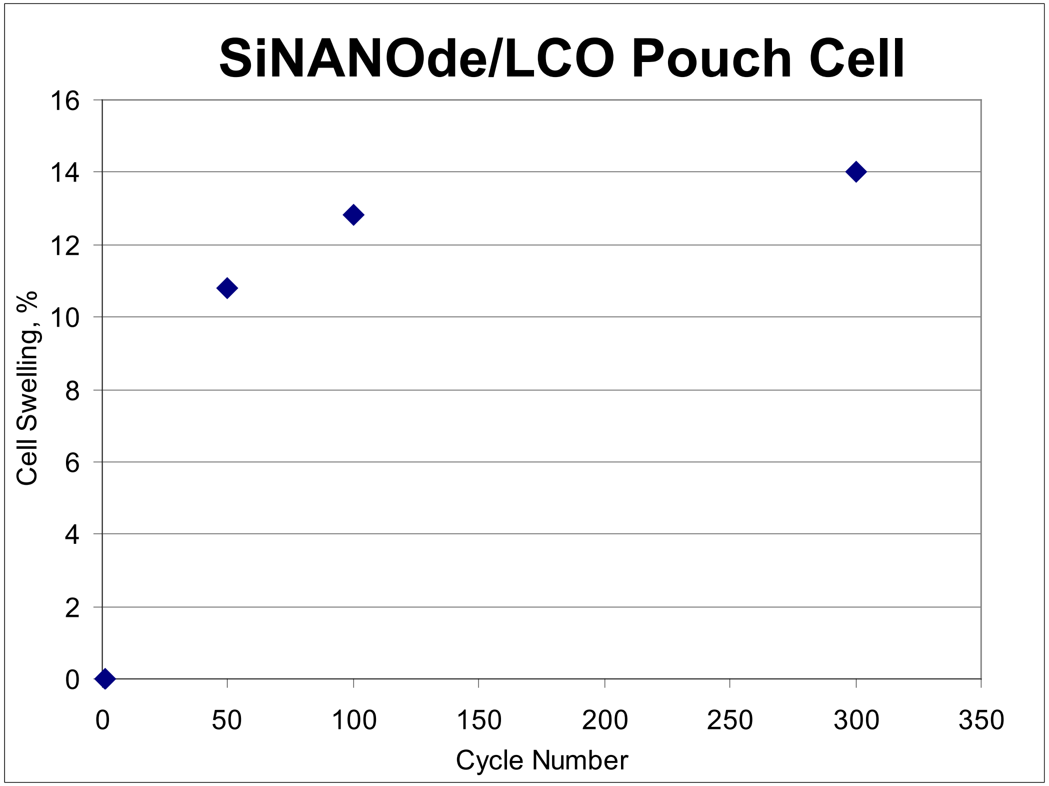




At 0.1C ~ 1C, SiNANOde pouch cell (Left) has a specific power similar to graphite pouch cell (Right).

At 4.5C, superior power performance can be achieved in the high energy density SiNANOde pouch cell.

# Technical Achievement
## - Cell Development

***Thickness change of High Energy Density Pouch Cells: SiNANOde/LCO*** after 300 cycles




- Pouch cells have showed acceptable cell thickness change, < 14% cell swelling over 300 cycles.

# Technical Achievement
## - Cell Development

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Self discharge and subsequent recharge is comparable (~1% less) than commercial graphite

| Condition | 8% SiNanode /LCO Normalized to Graphite/LCO Control |
|---|---|
| Retention % @20°C at end of 1 month | 99.6% |
| Realized capacity upon recharge after discharging at 20°C for 1 month | 98.7% |
| Retention % @60°C at end of 1 week | 98.7% |
| Realized capacity upon recharge after discharging at 60°C for 1 week | 99.3% |

# Collaborations

- A123 (Industry, within the VT program)
- LG CPI (Industry, within the VT program)
- LGC (Industry, within the VT program)
- Dow Kokam (Industry, within the VT program)
- Farasis Energy (Industry, within the VT program)
- University of California Berkeley/LBNL/NREL/ANL (University and US DOE Laboratories, within the VT program)

# Future Work

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## Focus on achieving high energy density and enhanced cycle life

***Cycle Life Enhancement for 700~1000 mAh/g Anode***
- Pilot-scale manufacturing quantities of SiNANOde product
- Cost-sensitivity modeling
- Optimize the SiNANOde and appropriate binders
- Develop electrolyte additives to improve cycle life
- Electrochemical analysis

***Enhanced Si Capacity 1,600 mAh/g Anode***
- Improve battery discharge rate performance
- Achieve high electrode loading
- Achieve a reversible specific capacity of 1,600 mAh/g

***Cell Performance Improvements***
- Optimize the cathode material composition
- Minimize inactive components in the cell
- Address electrode activation during cell formation cycles
- Evaluate the compatibility of the developed electrolyte and binder
- Improve the cell design to achieve high energy density and long cycle life
- Develop cell formation/testing protocol
- Evaluate cells at low temperature and appropriate voltage

# Summary

**Accomplishments**

- SiNANOde can be controlled in 500 ~ 1800mAh/g with an ICE of > 92%.
- 700~1000 mAh/g SiNANOde has been cycled 800 cycles at 79% retention in coin cell.
- 600mAh/g SiNANOde/LCO cell has >300 cycles or 600mAh/g SiNANOde/NCA cell has ~1000 cycles at 80% retention.
- LMR-NMC cathode achieves a reversible specific capacity of 275 mAh/g with an improved C-rate performance from 0.2C to >0.5C at high loading, which results in the pouch cells of 300~400Wh/kg coupled with 1200mAh/g SiNANOde.
- 550mAh/g SiNANOde/LCO pouch cells achieved 260Wh/kg and 600Wh/L. The pouch cells have showed acceptable cell thickness increase of < 14% over 300 cycles.
- We delivered the high energy density cells and PHEV cells to U.S. DOE for evaluation, which has unique specific power and low temperature performance.
- SiNANOde development has been extensively explored on various graphite/carbon powder substrates using low cost precursors, which lead to a cost effective production.
- SiNANOde cell's self discharge and subsequent recharge is comparable to commercial graphite cells.
- We have developed a new electrolyte C1.1 that enables higher coulombic efficiency and hence cycling performance for SiNANOde cell with electrolyte C1.1 better than that with previous electrolyte C1.

## Summarized achievements:

| | | | |
|---|---|---|---|
| **Anode Targets:** | 700-1000 mAh/g | >800 cycles | |
| **Anode Achievement:** | 700~1600 mAh/g | ~800 cycles | |
| **Cathode Targets:** | 250 mAh/g | >800 cycle | |
| **Cathode Achievement:** | >250 mAh/g | >200 cycles (ongoing) | |
| **Battery Targets:** | 350 Wh/kg | 800 Wh/L | <150 $/kWh (cell) |
| **Battery Achievement:** | 250~400 Wh/kg | 550~700 Wh/L (up to Si% and cathode) | |

# Acknowledgements

- *Team Battery at OneD Material (Nanosys), A123, and LGCPI/LG Chem.*
- *Support from the U.S. Department of Energy*